

TITLE
BRANCHED POLYOLEFIN SYNTHESIS

BACKGROUND OF THE INVENTION

5 Macromolecular engineering using commodity monomers is becoming a major trend in polymer technology to satisfy the demand for new properties, improved cost effectiveness, ecology and quality. Functional polymers with low molecular weight, low polydispersity, compact, branched structures and terminally-located reactive groups are
10 expected to exhibit superior performance/cost characteristics, by virtue of lower inherent viscosity and higher reactivity vs. conventional linear statistical copolymers.

 The terminally-functional branched polymers appear to be ultimate reactive substrates for networks, because the branch points can
15 substitute for a significant portion of expensive reactive groups and provide better distribution of the reactive groups. Polymers having large numbers of short branches below critical molecular weight are unlikely to form any entanglements and should exhibit low inherent viscosity and good flow even in concentrated solutions.

20 Conventional techniques for synthesizing well-defined branched polymers require expensive multistep processes involving isolation of reactive intermediate macromonomers. The macromonomers have polymerizable end groups, which are usually introduced using functional initiator, terminating or chain transfer agent. Well-defined
25 branched polymers are prepared by the macromonomer homopolymerization or copolymerization with suitable low molecular weight comonomer selected based on known reactivity ratios. These methods have been reviewed and only single-branch polymers from single incorporation of the macromonomers are reported; multiple
30 reincorporation of the growing macromonomers was never attempted, e.g., R. Milkovich, et al., U.S. Patent No.3,786,116; P. Remp, et al., Advan. Polymer Sci., 58, 1 (1984); J.C.Salamone, ed., Polymeric Materials Encyclopedia, Vol.3 and 4 (1996).

 Several linear macromonomers were prepared by end-capping
35 of living anionic polyolefins with unsaturated terminating agents providing polymerizable olefin end-groups, e.g., R. Asami et al., Macromolecules, 16, 628 (1983). Certain macromonomers have been incorporated into simple graft polymers by homo- or copolymerization with branched

structure not well-characterized and reincorporation of the macromonomers into more complex structures was not considered.

Dendrimers or hyperbranched polymers are conventionally prepared using expensive, special multifunctional monomers or expensive multistep methods requiring repetitive isolation of the reactive intermediates. Nothing in the prior art discloses synthetic conditions for production of macromonomers or polymers containing branches upon branches.

10 SUMMARY OF THE INVENTION

This invention relates to a general process for the synthesis of polyolefins containing branches upon branches and having polymerizable olefin end groups by a convenient one-pot polymerization of selected vinyl monomers with chain polymerization initiators and a method to provide olefin end groups by chain termination agents. The polymerization is carried out in such a manner that chain termination occurs gradually and each chain termination event terminates that particular polymer chain with polymerizable olefinic functionality. Subsequent reincorporation of the linear polymer chains produced early in the reaction leads to branching of subsequently-formed macromolecules which are terminated with polymerizable olefinic functionality. Subsequent reincorporation of the branched macromolecules leads to subsequently-formed polymer molecules containing branches upon branches which are terminated with polymerizable olefinic functionality. Spontaneous repetition of the process leads to highly branched or hyperbranched dendritic products still retaining polymerizable olefinic termini.

This invention concerns an improved process for the anionic polymerization of at least one vinylic monomer to form a branched polymer comprising contacting, in the presence of an anionic initiator:

- 30 (i) one or more anionically polymerizable vinylic monomers having the formula $\text{CH}_2=\text{C}\text{YZ}$, and
- (ii) an anionic polymerization chain terminating agent of formula $\text{CH}_2=\text{C}\text{Z-Q-X}$,

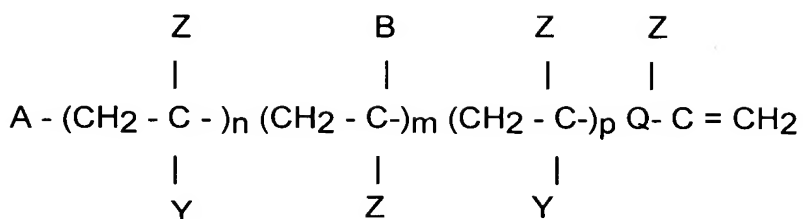
wherein:

- 35 Q is selected from the group consisting of a covalent bond, $-\text{R}'-$, $-\text{C}(\text{O})-$, and $-\text{R}'-\text{C}(\text{O})-$;
- Y is selected from the group consisting of R, CO_2R , CN, and NR_2 ;

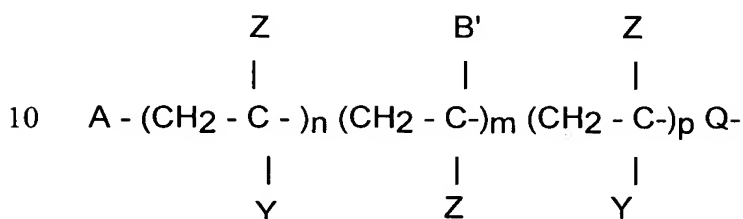
X is selected from the group consisting of halogen, and RSO_3 ;
 Z is selected from the group consisting H, R, and CN;
 R is selected from the group consisting of unsubstituted and
 substituted alkyl, vinyl, aryl, aralkyl, alkaryl and organosilanyl
 groups and R' is selected from the group consisting of
 substituted or unsubstituted alkylene, arylene, aralkylene,
 alkarylene and organosilanylene groups; the substituents being
 the same or different and selected from the group consisting of
 carboxylic acid, carboxylic ester, hydroxyl, alkoxy and amino;
 wherein the improvement comprises obtaining higher yields of
 branched polymer, the polymer having dense branch upon
 branch architecture and polymerizable vinylic chain termini,
 employing steps I, III, VI and at least one of II, IV and V:
 I. reacting (i) with an anionic initiator in a first step;
 II. decreasing the ratio of (i) to anionic initiator toward 1;
 III. adding (ii) optionally with some (i) in a second step;
 IV. selecting the rate of the (ii) addition, dependent on the (ii)
 reactivity;
 V. increasing the ratio of (ii) to anionic initiator toward 1; and
 VI. increasing the conversion of (i), (ii) and olefinic end
 groups from 70 to 100 %.

Based on the disclosure and Examples presented herein, one
 skilled in the art can select the optimum steps I -VII with minimum
 experimentation. One skilled in the art will also be able to select the
 appropriate anionic initiator and chain transfer agent for the monomer(s)
 being polymerized, by reference to the well-known conditions for anionic
 polymerization. Optionally, the process includes the step, VII, of
 converting anionic-growing end groups into non-polymerizable end
 groups. It is preferred to operate process step V at a ratio of about 0.7 to
 1, most preferably from 0.8 to 1. In step IV, the rate of addition will vary in
 the same direction as reactivity of (ii) so that addition will be relatively slow
 for less reactive component (ii) and will increase commensurate with
 increased reactivity of component (ii).

This invention further concerns the product of the above
 reaction which is composed primarily of a polymer having a branch-upon-
 branch structure and a polymerizable olefinic end group, having the
 structure:



where B =



B' = Y, B;

m = 1 to 100, preferably 1 to 20, more preferably 1 to 10; n = 0 to 100, preferably 0 to 50, more preferably 1 to 20; p = 0 to 100, preferably 0 to 50, more preferably 1 to 20; and n+m+p ≥ 2, preferably 5 to 50, more preferably 5 to 20;

if m > 1, then the m insertions are consecutive or not consecutive;

A = anionic initiator moiety selected from the group consisting of R; and

Q, Y, Z are as earlier defined.

More particularly, A = butyl, Z = H, and Y = Ph, Q = C₆H₄CH₂, W is CZ = CH₂, a composition of Claim 10 wherein W is a non-polymerizable moiety, or H.

Branch-upon-branch polymers (BUBP) are superior over straight branch polymers (SBP) in terms of more compact structure, reflected in lower inherent viscosity and better flow properties in melts and solutions for any given molecular weight of polymers. Therefore, BUBPs require less solvents and lower temperature than SBPs for processing.

BUBPs with terminal end groups are superior over SBP substrates by having much larger network fragments, which can be preformed and incorporated into new topology networks. BUBPs allow formation of new types of hybrid networks by combining different BUBPs with a good control on molecular level.

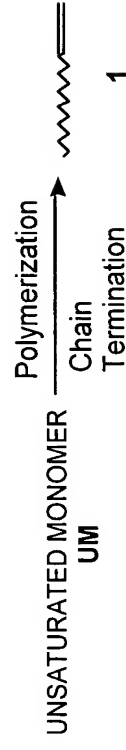
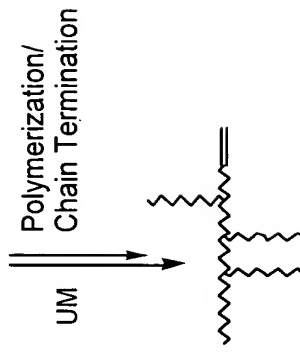
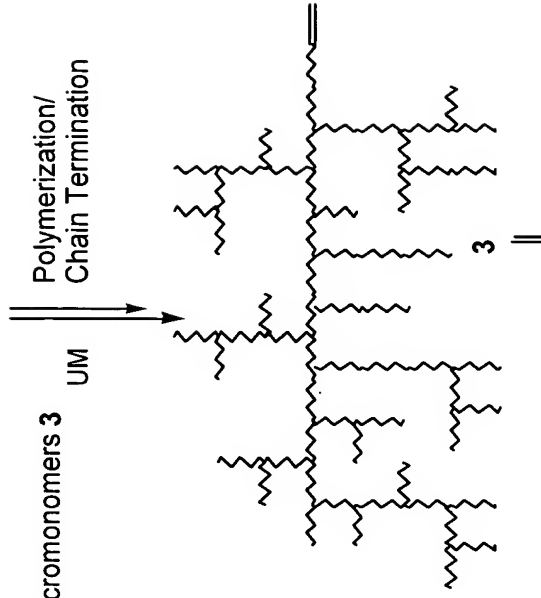
BUBPs allow incorporation of larger numbers of branch points per macromolecule, which are equivalent to curing sites. This improves

economy and conversion of reactive coatings by reducing the number of expensive curing sites.

5 In general, BUBPs offer at least a 10 percent improvement over SBPs of the same molecular weight in such characteristics as lower viscosity, reduced need for solvent, fewer curing sites in reactive substrates for networks and higher conversion of curing sites in final coatings, all of which provide better product stability.

DETAILS OF THE INVENTION

10 We have discovered a process for the synthesis of polyolefins containing branches upon branches and having polymerizable olefin end groups by a convenient one-pot polymerization of selected vinyl monomers with chain polymerization initiators and a method to provide olefin end groups by chain-termination agents. The polymerization is carried out in such a manner that chain termination occurs gradually and
15 each chain-termination event terminates that particular polymer chain with polymerizable olefinic functionality. The process is shown in Scheme 1.

Scheme 1**Step 1. Formation of linear macromonomers 1****Step 2. Formation of primary branched macromonomers 2****Step 3. Formation of branch-upon-branch macromonomers 3**

Subsequent incorporation of the linear polymer chains 1 produced early in the reaction leads to branching of subsequently-formed macromolecules terminated with polymerizable olefinic functionality 2. Subsequent reincorporation of the branched macromolecules 2 leads to polymer molecules containing branches upon branches 3 which are terminated with polymerizable olefinic functionality. Spontaneous repetition of the process leads to highly branched or hyperbranched dendritic products still retaining polymerizable olefinic termini.

The polymers made by the present process are useful in a wide variety of applications including coatings, processing aids in extrusion, cast, blown or spray applications in fiber, film, sheet, composite materials, multilayer coatings, photopolymerizable materials, photoresists, surface active agents, dispersants, adhesives, adhesion promoters, compatibilizers and others. End products taking advantage of available characteristics, particularly low inherent viscosity, can include automotive and architectural coatings having high solids, aqueous- or solvent-based finishes.

In a preferred process, the anionic initiator is selected from alkali metals, radical anions, alkyllithium and other organometallic initiating compounds, ester enolates, functionalized initiators, typical examples of which include: butyl-, methyl-, isopropyl-, phenyl-, vinyl-, allyl-lithiums, cumyl potassium, fluorenyl lithium.

Chain termination agents include p-vinylbenzyl chloride and bromide, p-vinylbenzyl tosylate, allyl chloride and bromide, vinyl dimethylchlorosilane, vinyl(chloromethyl)dimethylsilane, p-vinylphenyldimethylchlorosilane, methacryloyl chloride.

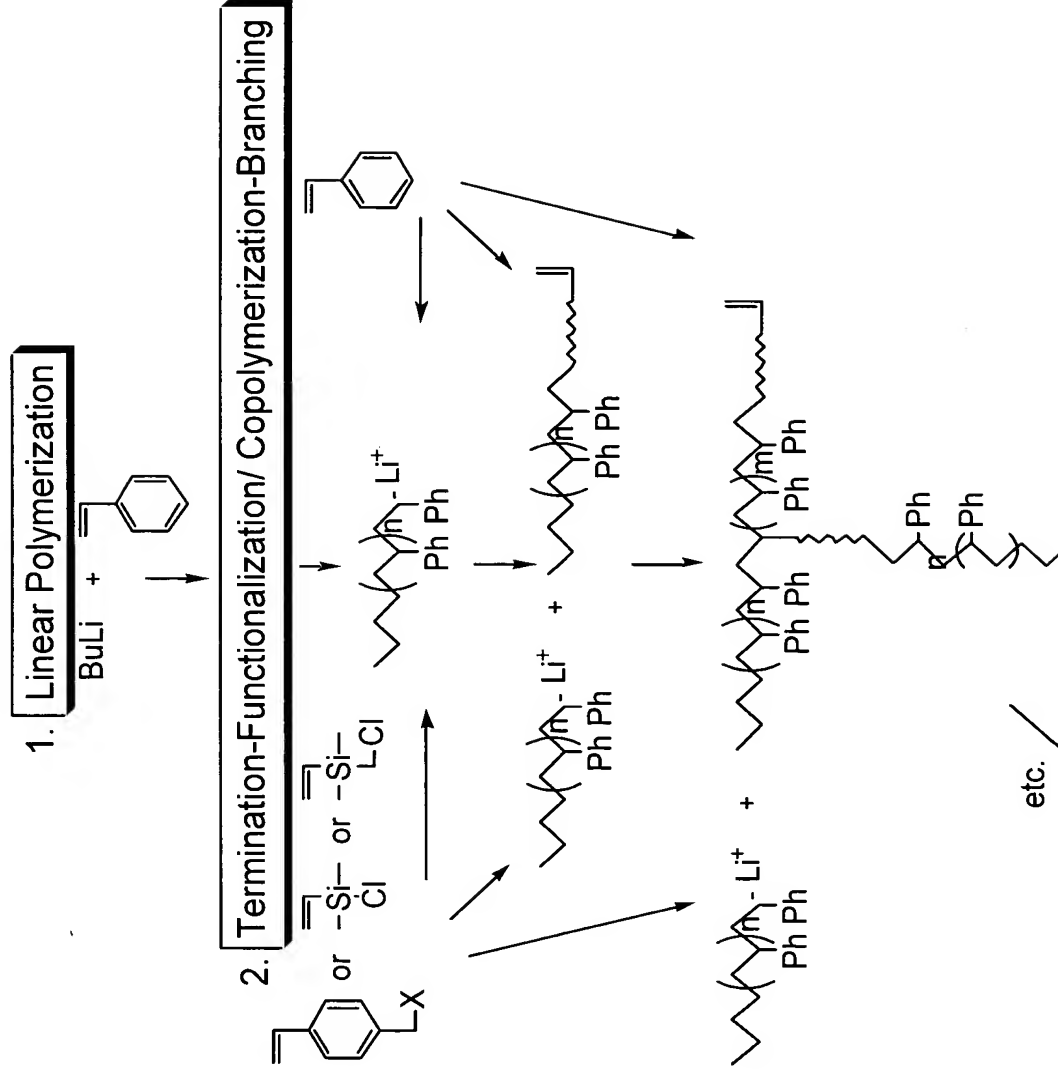
Substituents Q and X of the chain terminating agent are chosen to convey the appropriate reactivity in the terminating step and in anionic copolymerization of the desired monomer(s) under polymerization conditions.

The process can be conducted by bulk, solution, suspension or emulsion polymerization using batch or preferably starved feed reactor, which offers better process control.

The treelike dendritic branched polymers are formed by *in situ* generation and copolymerization of first linear and subsequently increasingly branched macromonomers through the polymerizable olefin group (Scheme 1). The method can be employed in anionic polymerization of styrene initiated by alkyllithiums, where dendritic

structures are formed by continuous addition of vinylbenzyl halides and/or vinylchlorosilanes acting as chain terminating/functionalizing/branching agents (Scheme 2). The data are consistent with a mechanism, in which the initially-formed linear macromolecules receive predominantly the vinyl end group through the termination by the vinylbenzylhalide or vinylchlorosilane. The vinyl reactive end group allows the linear macromonomer to participate in analogous subsequent (secondary) copolymerization steps leading eventually to even more branched structures ("branch upon branch" or dendrigrafts).

Scheme 2 - Synthesis of Dendritic Polystyrenes



Polystyrenes with molecular weights in the range 3,000 - 60,000, polydispersity <2.5 with 5 to 40 branches, each containing 3 to 30 monomer units were prepared, primarily controlled by the initiator/monomer/chain terminating agent ratio, relative addition rates, the reactivity ratios of the macromonomer and (co)monomers.

A chain polymerization is controlled by a chain termination step so as to provide a polymerizable olefin end group (Scheme 1). The branch upon branch structure is build by *in situ* generation and copolymerization of linear and subsequently increasingly branched macromonomers through the polymerizable olefinic group.

The monomer copolymerizability of $\text{CH}_2=\text{CYZ}$ primarily determined by the steric and electronic properties is well documented in the art. The chain process can involve either one or several different comonomers and is preferably anionic but can also be cationic or radical. Typical monomers include monoolefins, preferably styrene, α -methyl styrene, substituted styrenes, substituted styrenes with protected functional groups, vinyl aromatics, vinylpyridines, conjugated dienes, vinyl silanes, acrylates, methacrylates, acrylonitrile, vinylidene cyanide, alkyl cyanoacrylates, methacrylonitrile, vinyl phenyl sulfoxide, vinyl aldehydes, vinyl ketones and nitroethylenes.

The data are consistent with a mechanism, in which the initially-formed branched macromolecules 2 receive predominantly the olefin end group through the chain termination. See Scheme 1. Having a reactive olefin end group allows 2 to participate in analogous subsequent (secondary) copolymerization steps leading eventually to branch-upon-branch polymers, 3.

Formation of branch-upon-branch structures 3 is indicated by the significant increase (up to 50 x) in the polymer molecular weight compared to the control experiments where the same monomer/ initiator ratios but nonolefin chain terminating agents such as benzyl chloride or methanol are used instead of the p-vinylbenzyl chloride.

In general, vinylsilane terminated macromonomers show much lower reactivities toward homo- and co-polymerizations under the conditions studied, leading to polymers with lower molecular weight and less branched structures.

Branched structures of copolymers 3 are confirmed by very low inherent viscosities, values of "a" coefficient in Mark-Houwink equation, $[\eta] = K M^a$, falling in the range 0.18-0.66 vs. 0.72 for linear polystyrenes,

branching factors approaching 0.4 and the RMS radius less than a half of the linear analog of the same molecular weight in the range 10^5 - 10^6 as measured by GPC with a dual RI/LS detector.

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EXAMPLES 1 to 41

Preparation of Branch-Upon-Branch Polystyrenes Using p-Vinylbenzyl Chloride as Chain-Terminating Agent

The procedure of Scheme 2 illustrates the preparation and analysis of the branch-upon-branch polymer architecture by a multi-step/one-pot process. Formation of the branch-upon-branch architecture is determined by type of monomer and chain terminating agent (CTA), and by initiator concentration and rate of monomer and CTA addition. The expression "Ph" is used as an abbreviation for phenyl, "PSty" as an abbreviation for polystyrene and "PhMe" is an abbreviation for toluene.

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EXAMPLE 1

Polymerization of Styrene with p-Vinylbenzyl Chloride as a Chain-Terminating Agent.

<u>Part</u>	<u>Ingredient</u>	<u>Amount</u>
I	THF	10 ml
	styrene	2 g
II	BuLi (2.0 M in hexane)	1 g
III	p-vinylbenzyl chloride	0.25 g
	styrene	0.75 g

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Part I was charged into the dry reactor equipped with a magnetic stirrer and nitrogen-positive pressure, and cooled to -78°C in a dry ice/acetone mixture in a dry-box. After 15 min., Part II (BuLi) was added at once and the reactor contents were held at -78°C for an additional 20 minutes. Then, Part III was fed gradually over 5 min. The reactor contents were held at -78°C for an additional 35 minutes. About 0.5 g of sample was withdrawn followed by GC determination of the styrene and p-vinylbenzyl chloride concentrations. Volatiles were stripped on a rotovap. The polymer was dissolved in methylene chloride, filtered through a silica and volatiles were stripped on high vacuum for several hours and the oligomers/polymers were analyzed by NMR and GPC. Yield 3.0 g, $M_n = 31,600$, $M_w/M_n = 2.37$ vs. linear PSty in tetrahydrofuran (THF) by GPC. Decane was used as an internal GC standard and molar

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response factors were determined using mixtures of known composition containing styrene, p-vinylbenzyl chloride and decane. Polymer composition was followed by Matrix Assisted Laser Desorption Ionization (MALDI) Mass Spectroscopy. Polymer molecular weight was measured by GPC using RI, LS and viscosity detectors. Structure of the polymers, including branching density and end groups, was characterized (see Examples 42 to 46) by ^1H and ^{13}C NMR, MALDI, light scattering, GPC with dual RI/capillary viscometry and RI/LS detectors.

EXAMPLES 2 TO 11

Synthesis of dendritic polystyrenes from BuLi, styrene, vinylbenzyl chloride (VBC), and linear analogs using either benzyl chloride (BC) or benzyl bromide (BB) in cyclohexanes (CHE), THF or in toluene at room temperature. M_n and M_w/M_n by GPC in THF vs. PSty standards; styrene added at once to BuLi/THF in the 1st step; and commercial grade substrates used without purification. See Table 1 for results.

TABLE 1

<u>Example</u>	BuLi (mmol)	Sty (mmol) (1 st + 2 nd steps)	CTA (mmol)	Solvent (ml)	M _n (GPC)	M _w /M _n (GPC)	M _n /th. ^a linear	T _g (°C)	Yield (g)
2	3.040	1.92	1.97 (VBC)	1.1 CHE	17,000	2.39	240		0.14
3	0.912	28.8+1.92	0.655 (VBC)	5 THF	31,700	2.38	3,680	90	2.8
4	6.080	3.84	5.24 (VBC)	1 THF	19,300	2.11	240		0.1
5	3.040	19.2 + 1.92	1.97 (VBC)	5 THF	13,900	4.70	898	73	2.6
6	3.040	19.2 + 1.92	2.37 (BC)	5 THF	12,800	2.65	871	71	2.5
7	0.912	1.92	0.655 (VBC)	3 PhMe	6,600	3.86	393		0.16
8	3.040	19.2 + 1.92	1.97 (VBC)	5 PhMe	12,900	3.46	898	72	2.6
9	6.080	19.2 + 5.76	3.93 (VBC)	5 PhMe	17,200	5.01	602	74	2.1
10	9.12	19.2 + 9.60	6.55 (VBC)	5 PhMe	7,800	5.51	503	55	1.1
11	9.12	19.2 + 9.60	7.90 (BC)	5 PhMe	5,700	1.36	476	53	2.3

a) M_nth = Sty(g)/BuLi (mole) + 57 + MW (CTA) - MW (halogen)

Examples 12 to 31

5 Synthesis of dendritic polystyrenes from BuLi, styrene, vinylbenzyl chloride (VBC), vinylbenzyl bromide (VBB), and linear analogs using either benzyl chloride (BC) or benzyl bromide (BB), or methanol in THF at -78°C. M_n and M_w/M_n by GPC in THF vs. PSty standards; BuLi added at once to styrene/solvent in the 1st step; and commercial grade substrates were dried over molecular sieves. See Table 2 for results

TABLE 2

Example	BuLi (mmol)	Sty (mmol) (1 st + 2 nd steps)	CTA (mmol)	THF (ml)	M _n (GPC)	M _w /M _n (GPC)	M _n /th. ^a)	T _g (°C)	Yield (g)
12 ^b)	3.04	19.2 + 5.76	1.97 (VBC)	5	31,300	4.23	1,029	88	2.6
13 ^b)	3.04	19.2 + 5.76	2.37 (BC)	5	5,800	2.84	1,002	33	2.9
14 ^b)	3.04	19.2 + 5.76	1.64 (VBC)	5	48,100	5.67	1,029	95	2.7
15 ^b)	3.04	19.2	9.38 (MeOH)	10	3,400	2.76	743	47	2.1
16	3.04	19.2	1.97 (BC)	10	3,700	2.83	832	58	2.1
17	3.04	19.2	1.64 (VBC)	10	23,300	1.93	859	89	2.2
18	3.04	19.2 + 7.20	1.64 (VBC)	10	31,600	2.37	1,079	88	3.0
19	3.0	32.1 + 19.2	2.29 (VBC)	13.3	37,900	1.93	1,954	93	4.0
20	3.0	32.1 + 28.8	2.62 (VBC)	13.3	42,900	3.08	2,287	94	5.8
21	3.0	3.5 + 38.4	2.62 (VBC)	13.3	58,200	2.95	2,621	95	6.3
22	3.0	22.3	2.62 (VBC)	17.4	37,700	1.90	949	92	2.6
23	3.0	22.3 + 19.2	2.62 (VBC)	17.4	48,700	2.42	1,616	92	3.9
24	3.0	22.3 + 19.2	2.49 (VBC)	17.4	51,300	2.31	1,616	94	4.2
25	3.0	5.58	2.62 (VBC)	4.4	23,300	2.70	368	86	0.8
26	3.0	22.3	2.78 (VBB)	17.4	10,200	4.54	949	72	2.9
27	3.0	22.3 + 19.2	2.64 (VBB)	17.4	9,800	8.10	1,616	81	4.1
28	3.0	28.2 + 19.2	2.95 (VBC)	11.8	29,000	3.14	1,821	84	4.7
29	3.0	22.3	2.53 (BC)	17.4	4,100	2.53	923	49	2.6
30	3.0	22.3 + 38.4	2.49 (VBC)	17.4	47,100	2.40	2,284	93	5.3
31	3.0	22.3 + 67.2	2.49 (VBC)	17.4	50,000	2.98	3,284	90	8.4

a) M_nth = Sty(g)/BuLi (mole) + 57 + MW (CTA) - MW (halogen)b) Styrene added at once to BuLi/solvent in the 1st step.

Examples 32 to 41

Approaches to dendritic polystyrenes from BuLi, styrene, vinylchlorodimethylsilane (VCD) or vinyl(chloromethyl)dimethylsilane (VCM) in THF at -78°C. M_n and M_w/M_n by GPC in THF vs. PSty standards; BuLi added at once to styrene/solvent in the 1st step; and commercial grade substrates dried over molecular sieves. See Table 3 for results.

TABLE 3

Example	BuLi (mmol)	Sty (mmol) (1 st + 2 nd steps)	CTA (mmol)	THF (ml)	M _n (GPC)	M _w /M _n (GPC)	M _n /th. ^a linear	T _g (°C)	Yield (g)
32*	3.04	19.2 + 9.60	2.49 VCD	1(+9)	3,200	1.61	1,129	51	3.4
33	3.04	19.2 + 9.60	2.07 VC	10	5,500	3.22	1,129	68	3.1
34	3.0	32.5 + 28.8	2.90 VCD	11.3	6,700	2.48	2,272	76	6.7
35	3.0	22.3	2.49 VCD	17.4	4,800	2.19	917	71	2.3
36	3.0	22.3 + 19.2	2.90 VCD	17.4	6,500	2.19	1,584	72	4.2
37	3.04	19.2	2.60 VCM	10	8,400	3.17	841	70	2.3
38*	3.04	19.2	2.60 VCM	1 (+9)	2,100	1.70	841	25	2.5
39*	2.04	19.2 + 9.60	2.60 VCM	1 (+9)	3,300	1.80	1,143	38	3.2
40	3.0	32.5	2.97 VCM	11.3	9,400	3.04	1,286	74	3.8
41	3.0	22.3 + 19.2	2.97 VCM	17.4	6,200	2.22	1,598	71	4.4

a) M_nth = Sty(g)/BuLi (mole) + 57 + MW (CTA) - MW (halogen)

*In 1 ml THF + 9 ml PhMe at room temperature.

EXAMPLES 42 to 46

Demonstration of Branched Structure of Polystyrenes Prepared Using p-Vinylbenzyl Chloride as Chain-Terminating/Branching Agent

- 5 Branched structures were confirmed by very low inherent viscosities, low "a" coefficient in the Mark-Houwink equation falling in the range 0.18-0.66 vs. 0.72 for linear polystyrenes and branching factors approaching 0.4. See Table 4.

Table 4
Characterization of Branching in Dendritic Polystyrenes

Example	IV ^a	LS ^b	M _w	M _η ^c	M _w ,LS ^e	M _η ,SEC ^e	M _w /SEC ^e	g ^{'d}	g _w ' ^c	a ^c
Control (Linear PSty)	0.22		34,500		1.03					0.72
42	0.28	88,300 ^b	79,000 ^b	71,100	0.66	0.77	0.72	0.87		0.66
43	0.19	81,000 ^b	80,000 ^b	63,000	0.48	0.57	0.48	0.63	0.18	
44	0.20		87,800				0.48			
45	0.22		83,800				0.56			
46	0.28		188,700				0.39			

a) measured in THF via capillary viscometry

b) measured in PhMe

c) SEC viscometry with universal calibration

d) $g' = ([\eta]b/\{\eta\})_M = [\eta]b/K_{MB}^a$

e) $a = 0.725$, $K = 11 \times 10^{-5}$ (for linear PSty)